

96 COMMERCIAL PROCESSES FOR THE MANUFACTURE OF SUPERABSORBENT POLYMERS

Even when the comminution and transport operations are selected to minimize the production of unwanted fine-particle size fractions, their handling and disposition must be considered. The patent record shows that superabsorbent manufacturers realized, after the fact, that the unwanted fines fraction needs to be managed. One solution is to simply remove the fines from the product by screening. That, however, only postpones the question of what to do with them. Two paths are discussed.

The first path attempts to transform the fines into a second product or to include them as an inert or active filler in a second product.⁸⁴⁻⁸⁹ This path is not discussed in this volume. The second path is to recycle the superabsorbent fines into the primary superabsorbent product. In one case, fines, water, and fresh gel (direct from the reaction step) are physically blended to yield a uniform blended product.^{14,15} About 15% fines, based on the weight of the final dried product, are blended. Fines of partially neutralized product can be rehydrated, without substantial agglomeration or gel-blocking, by using a high speed mixer, followed by mixing of the hydrated fines with fresh gel.¹⁴ (Similar equipment is described for the addition of reactive additives for advanced generation products.⁹⁰⁻⁹²) Also, recycle of fines to a gel stream consisting of the fines, fresh gel (un-neutralized), and a few parts of water processes more easily than the fresh gel.¹⁵ The mixture of hydrated fines and fresh gel is extruded through a die so that the gel is formed into "shapes having sufficient surface area for drying."¹⁴

Unless a reaction takes place between the hydrated fines and the gel, for example by using a reagent such as ethylene glycol diglycidyl ether, the fines are not chemically bound to the gel polymer. As a consequence,¹⁷ the product may not retain its "unitary nature under the stresses imposed by hydration." Viewing the swelling of agglomerated particles under a microscope shows that the agglomerated larger particles break into its fine-particle components as the mass swells.

Recycle of superabsorbent fines to the polymerization step is also described. In this art, the fines are swollen with monomer or monomer solution and the mixture polymerized.^{16,17,29,93} In one case,¹⁶ the monomer is first added to the reactor, followed by addition of the fines. Although the viscosity of the monomer mix increases substantially with the addition of fines, no particular problems were noted. Equipment to mix fines and monomer is not described in these patents. However, equipment of the type used to swell fines with water might be useful at a commercial scale.⁹⁴ Equipment necessary for polymerizations containing fines¹⁶ is similar to the reaction vessels previously described.^{32,33} When polymerizing on a continuous belt, fines were added to the belt polymerizer as a part of the monomer mix.²⁹ In this case, the fines are first mixed with a nonswelling solvent, a nonswelling salt solution, or a nonswelling monomer such as acrylic acid and then added to an aqueous solution of monomer. The amount of fines that can be added may be as high as 50%,¹⁶ but is probably more on the order of 20% or less.^{16,17,29} When fines are recycled to the polymerization, product properties are nearly equivalent to properties of products made without fines recycle. However, in one case for polymers of the same swelling capacity, a slight reduction in absorbency under load was noted.¹⁷

Available Copy

3.2. SOLUTION POLYMERIZATION 97

3.2.8. Addition of Post-Treatments

3.2.8.1. Advanced Products. The processes described above produce a particle with crosslinking that may be assumed to be essentially uniform throughout the particle. As such, the swelling and modulus behavior of the product particles can be described by theories of network swelling and elasticity (see Chapter 5). One problem associated with these superabsorbent polymers was also recognized in a variety of water soluble polymers, e.g., poly(acrylamide), cellulose ethers,⁹⁵ or soluble poly(acrylic acid).⁹⁶ This problem is the tendency of the granular polymers to clump, "gel block," or form fish-eyes when aqueous liquids are added to them or they are added to aqueous liquids. The surfaces of the massed particles swell rapidly to form a soft, deformable layer. The resulting particle deformation and interparticle adhesion reduces interparticle porosity and limits the swelling rate of the polymer mass to the diffusion rate of liquid through the partially swollen mass.

The first attempts to solve this problem in highly absorbent anionic polyelectrolytes used multivalent cations to form a crosslinked surface layer that was more rigid than the original core polymer.⁹⁷ Subsequently, to give products with improved dispersibility and absorption rate, the surface of crosslinked polyacrylate particles was reacted with a variety of multifunctional organic compounds.^{49,50,98,99} This structural improvement is shown schematically in Figure 3.9. Swelling capacity data as a function of particle size readily demonstrate that a shell of real, as opposed to infinitesimal, thickness is formed by surface crosslinking processes. The shell of higher crosslink density provides a more rigid surface layer during swelling and prevents the gel-blocking that would otherwise occur early in the swelling process (Chapter 5). As a result, liquid can flow through the bed of particles to each particle, increasing the effective surface area available for swelling and the apparent swelling rate. The swelling and modulus behavior of structured particles are discussed in Chapter 5.

Because a surface layer is formed on each individual particle, the crosslinking reaction, but not necessarily the reagent addition, must occur after achieving the desired particle size distribution. Any compound that can react with two or more functional groups on the polymer backbone can function as a surface crosslinking reagent. For superabsorbents, this requires reagents that can react with the car-

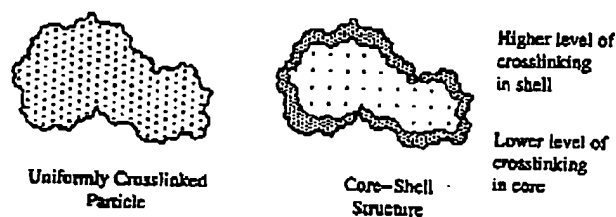


Figure 3.9. Schematic representation of a uniformly crosslinked superabsorbent particle and a structured particle with a surface layer of higher crosslink density.

Best Available Copy

3.2. SOLUTION POLYMERIZATION 99

tween structured polymers made under different sets of process conditions. For example, Tsubakimoto et al.⁹⁰ showed that a water/alcohol carrier for the surface crosslinking reagent yields a structured polymer with less fish-eye formation than when the reagent is added undiluted. Later, more sophisticated tests (see Chapter 4, section 4.6.4) that measure swelling under a compressive load (absorbency under load) were able to quantitatively distinguish between structured polymers made under different sets of process conditions. Results of these tests suggest that penetration of the reagent into the particles and control of the dispersion of the crosslinking agent over the surface of the particles are critical process considerations for achieving success in the absorbency under load test.

Optimization of the surface crosslinking process to reduce gel-blocking in an absorbency under load test has been addressed in a number of ways. Surface crosslinking reagents have been added in aqueous solutions and other diluents such as alcohol or aqueous salt solutions.^{102,103} However, there are several difficulties with these approaches.¹⁰⁶ Water swells the particle surface and lowers the glass transition temperature of the polymer at the surface, increasing penetration of the surface crosslinking agent into the polymer particle. However, excessive amounts of water cause the polymer to swell and can make handling difficult. Inorganic particulates, such as silicates, in addition to controlling the hydrophilic/hydrophobic balance of the treatment reagent, are used, in combination with high-speed blending of the reagents with the polymer, to control agglomeration during the reagent addition process.^{90,99} The alcohol or salt solution helps disperse the surface crosslinking agents over the powder by diluting the crosslinker (larger volume) and helps control or prevent agglomeration of the powder by reducing the activity of water in the solution. The use of an organic solvent has the obvious disadvantage of requiring recovery and recycle. Also, for example with the lower alcohols, the low flash points require extra equipment and more safeguards to maintain safe operation.

Adding 0.2 wt% glycerol, in combinations of water and *n*-propanol, to a 65% neutralized polyacrylate made by the process of Siddall and Johnson²⁸ shows the effect of reagent penetration. One gram of liquid was added to 100 g of polymer powder. Twenty-five grams of the reagent treated polymers was heated in an aluminum dish for 15 min at 200°C in a preheated circulating-air oven equipped with a steel plate as a heat sink. Table 3.5 shows the swelling capacity (method described in Chapter 4, section 4.6.1.2) and absorbency under load (described in Chapter 4, section 4.6.4.2) data. Swelling capacity decreases as the amount of water in the reagent solution increases. Similar results have been obtained by using aluminum acetate, ethyleneglycol diglycidyl ether, or ethylene carbonate as the surface crosslinking reagent. This has been interpreted as resulting from increased penetration of the reagent into the particle and increased crosslinking throughout the particle rather than just on the surface.

Other process choices also affect the resulting properties. Table 3.5 suggests that for glycerol the optimum weight ratio of water to *n*-propanol is about 30:70 (based on the values of swelling capacity and absorbency under load). The amount of water may be reduced by choosing a more hydrophilic organic solvent such as methanol. Increasing the salt concentration of the crosslinker solution also decreases the hy-

351 multiple Copy

100 COMMERCIAL PROCESSES FOR THE MANUFACTURE OF SUPERABSORBENT POLYMERS

Table 3.5. The effect of solvent hydrophilicity on the properties resulting from surface crosslinking of a polyacrylate treated with 0.2 wt% glycerol and then heated at 200°C for 15 min

Solvent Composition Water/ <i>n</i> -propanol (w/w)	Swelling Capacity (g/g)	Absorbency Under 2.0 kPa Load (g/g)
Starting material	39.0	9.0
0/100	36.4	23.2
10/90	35.0	21.6
20/80	34.7	29.0
30/70	28.8	29.3
40/60	30.5	29.3
50/50	29.3	28.6

hydrophilicity of the solution (reduced particle surface swelling) and has the expected effect on product quality. The amount of crosslinker solution and the concentration of crosslinker in the solution also impact the results. When too little crosslinker solution is used, for example to avoid agglomeration, the particle surface coverage can be incomplete, leading to increased gel-blocking in the swelling under load tests. When the concentration of crosslinker is too low, or an insufficient quantity of reagent is applied, the amount of additional crosslinking at the surface does not make the surface sufficiently rigid to give the required resistance to gel-blocking.

More recently, the desire for products with an improved combination of swelling capacity and absorption under load^{107,108} has led to more complex surface crosslinking systems.^{100,106,109} In one case,¹⁰⁰ a shell structure is achieved by using two surface crosslinking reagents with different solubility parameters, one greater than 12.5 (cal/g³)^{1/2} and the other less than 12.5 (cal/g³)^{1/2}. The combination of solubility parameter and low molecular weight of the crosslinking reagents (less than 350 g/mol) is said to optimize the penetration of the surface crosslinking reagent into the particle (compare row 4 to rows 2 and 3 of Table 3.6). In a second case, surface crosslinking with a specific class of high-molecular-weight (greater than 1,000 g/mol) azetidinium compounds leads to polymer particles with more ideal shell thicknesses (less than 10% of the particle radius).¹⁰⁹ The high molecular weight of the reagent limits the penetration of the crosslinking agent into the particle so that the swelling capacity is not reduced too greatly. A range of surface tension, about 40–50 dynes/cm, of the applied crosslinker solution promotes spreading of the crosslinker solution over the surface of the particles.¹¹⁰ A two-step addition of surface crosslinking agent also leads to improved properties.¹¹¹ Another two-part process, in which a first crosslinker (hydrophilic polymer or metallic compound) is reacted with a second additive on the surface of a wet polymer (10–100 parts), has also been described. The extent of hydration of the polymer and crosslinker are chosen to give the desired penetration of the surface crosslinking reagents into the particle and the desired combination of properties. The process seems most suitable for suspension-made polymers, but its inventors claim its utility is for polymers made by solution polymerization. In one example, a coating of poly(ethyleneimine)

Not Available Copy